Taylor Expansions of UCC

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Unitary Coupled Cluster Theory

- Coupled cluster theory is (kind of) accurate and size-consistent, but non-variational
- Unitary coupled cluster (UCC) is variational, but classically intractable
- Its Trotterized form(s) can be implemented on quantum hardware

$$|\psi_{CC}\rangle = e^{\hat{T}} |0\rangle$$

$$\text{Make ansatz unitary} \downarrow$$

$$|\psi_{UCC}\rangle = e^{\hat{T}-\hat{T}^\dagger} |0\rangle$$

$$\text{Trotterization} \downarrow$$

$$|\psi_{tUCC}\rangle = \left(\prod_{ij\ldots}^{ab\ldots} e^{\left(t_{ab\ldots}^{ij\ldots} \hat{a}_{ij\ldots}^{ab\ldots} - \text{H.C.}\right)} \right) |0\rangle$$

2nd-Order UCCSD

- BCH Expansion of UCC:

$$
\begin{aligned}
E_{UCCSD} =& \langle H \rangle + \langle [\hat{H}, \hat{T} - \hat{T}^{\dagger}] \rangle + \langle [[\hat{H}, \hat{T} - \hat{T}^{\dagger}], \hat{T} - \hat{T}^{\dagger}] \rangle, \ldots \\
=& E_{ref} + 2 \langle 0 | \hat{H}_N \hat{T} | 0 \rangle + \langle 0 | \hat{T}^{\dagger} \hat{H}_N \hat{T} | 0 \rangle \\
&+ \langle 0 | \hat{H}_N \hat{T}^2 | 0 \rangle - \langle 0 | \hat{H}_N \hat{T}^{\dagger} \hat{T} | 0 \rangle + \ldots
\end{aligned}
$$

- Truncating at second order in $\hat{T}$ and only including singles and doubles yields the Simons-Hoffmann "SHUCC" equations for minimizing the energy. For canonical orbitals:

Not in LCCSD

$$
0 = [\hat{H}_N \mathbf{t}]^i_a + \boxed{\sum_{ijab} \langle 0 | \hat{H}_N | \phi^{ab}_{ij} \rangle \, t^j_b}
$$

$$
- \langle 0 | \hat{H}_N | \phi^{ab}_{ij} \rangle = [\hat{H}_N \mathbf{t}]^{ij}_{ab}
$$

Why Does This Look Like LCCSD?

- Linearized coupled cluster (LCC) usually refers to variational minimization of a linearized version of the CC functional:

$$\epsilon[\mathbf{t}, \boldsymbol{\lambda}] = E_{ref} + \langle 0|(1+\hat{\Lambda})[H_N(1+\hat{T})]_C|0\rangle$$

- For an HF reference with only singles and doubles, $\hat{\Lambda} = \hat{T}^\dagger$ and we get a similar linear stationary condition

$$0 = [\hat{H}_N \mathbf{t}]_a^i$$
$$-\langle 0|\hat{H}_N|\phi_{ij}^{ab}\rangle = [\hat{H}_N \mathbf{t}]_{ab}^{ij}$$

Commonalities (For Canonical Orbitals)

- Both LCCSD and SHUCCSD are size-consistent
- For STO-3G H_2, singles are irrelevant, so the methods are equivalent and amount to solving a two-level problem:

$$E_c = -\frac{|\langle ij||ab\rangle|^2}{E_1 - E_0}$$

- E_c diverges as the energies of $|0\rangle$ (E_0) and $|\phi_{ij}^{ab}\rangle$ (E_1) become degenerate

Epstein-Nesbet UCC

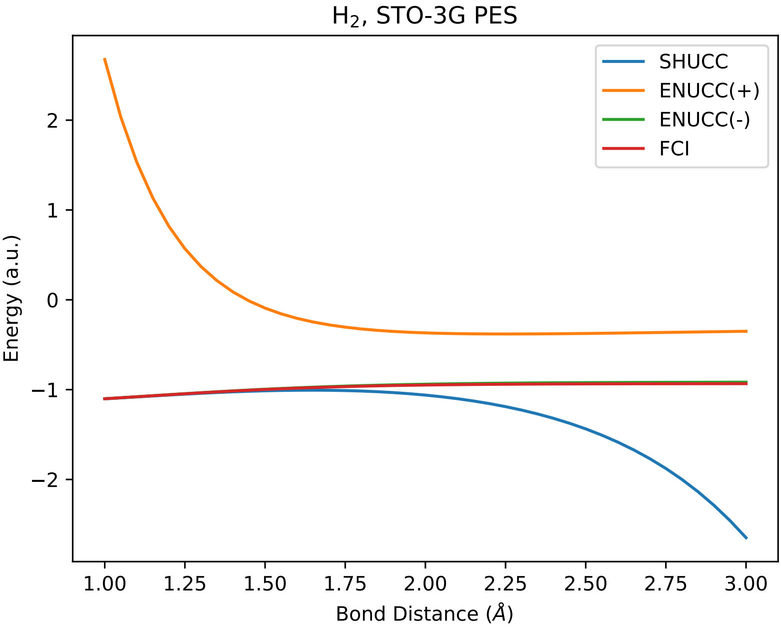
- We can include "diagonal" terms up to third order in $\hat{T}$ to treat degenerate systems. For canonical orbitals:

$$\epsilon_{ENUCC} = \epsilon_{SHUCC} - \frac{4}{3}\sum_{i<j}^{a<b} \langle ij||ab\rangle \left(t_{ab}^{ij}\right)^3$$

- When $|\phi_{ij}^{ab}\rangle$ and $|0\rangle$ approach degeneracy, this gives finite stationary H_2 energies:

$$E = E_0 \pm \frac{2\sqrt{2}}{3}\langle ij||ab\rangle$$

- The high-energy ENUCC solution appears to diverge in the weakly coupled regime, but the low-energy solution does not



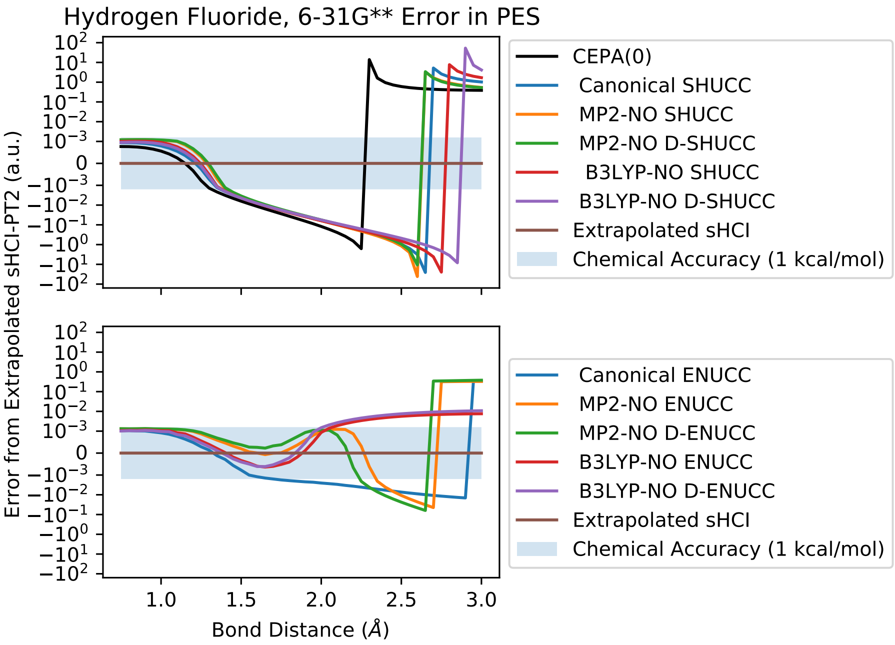
H_2, STO-3G PES
SHUCC
ENUCC(+)
ENUCC(-)
FCI
Energy (a.u.)
2
1
0
−1
−2
1.00
1.25
1.50
1.75
2.00
2.25
2.50
2.75
3.00
Bond Distance (Å)

Non-Brillouin Singles

- Both SHUCCSD and ENUCCSD become size-inconsistent if we mix the occupied and virtual canonical orbitals
- We can define disentangled (D-) SHUCCSD and ENUCCSD to avoid this, redefining the energy functional as:

$$\epsilon[\mathbf{t}] = \langle 0| e^{-\hat{T}_2+\hat{T}_2^\dagger} e^{-\hat{T}_1+\hat{T}_1^\dagger} \hat{H} e^{\hat{T}_1-\hat{T}_1^\dagger} e^{\hat{T}_2-\hat{T}_2^\dagger} |0\rangle$$

- Equivalently, we could define the ansatz as any Trotterized UCCSD ansatz where the singles are all closer to $\hat{H}$ than the doubles
- It might also be possible to understand D-SHUCCSD as a Newton step toward orbital-optimized UCCD


Hydrogen Fluoride, 6-31G** Error in PES
Error from Extrapolated sHCI-PT2 (a.u.)
Bond Distance (Å)
CEPA(0)
Canonical SHUCC
MP2-NO SHUCC
MP2-NO D-SHUCC
B3LYP-NO SHUCC
B3LYP-NO D-SHUCC
Extrapolated sHCI
Chemical Accuracy (1 kcal/mol)
Canonical ENUCC
MP2-NO ENUCC
MP2-NO D-ENUCC
B3LYP-NO ENUCC
B3LYP-NO D-ENUCC
Extrapolated sHCI
Chemical Accuracy (1 kcal/mol)

Understanding ENUCC

- Ignoring the singles for simplicity, ENUCC bears a similarity to the non-averaged CEPA variants, e.g. Malrieu's (SC)^{2}CI:

$$\frac{1}{4}\sum_{klcd} \langle \phi_{ij}^{ab} | \hat{H}_N | \phi_{kl}^{cd} \rangle \, t_{cd}^{kl} - \frac{1}{4}\sum_{klcd}^{EPV} \langle kl || cd \rangle \, t_{cd}^{kl} t_{ab}^{ij} = - \langle ij || ab \rangle$$

- Only summing over terms where the occupied orbitals violate the exclusion principle gives CEPA(3)
- Only including the term in the summand where **every** orbital is EPV-violating gives the ENUCC stationary condition (down to a factor of 2):

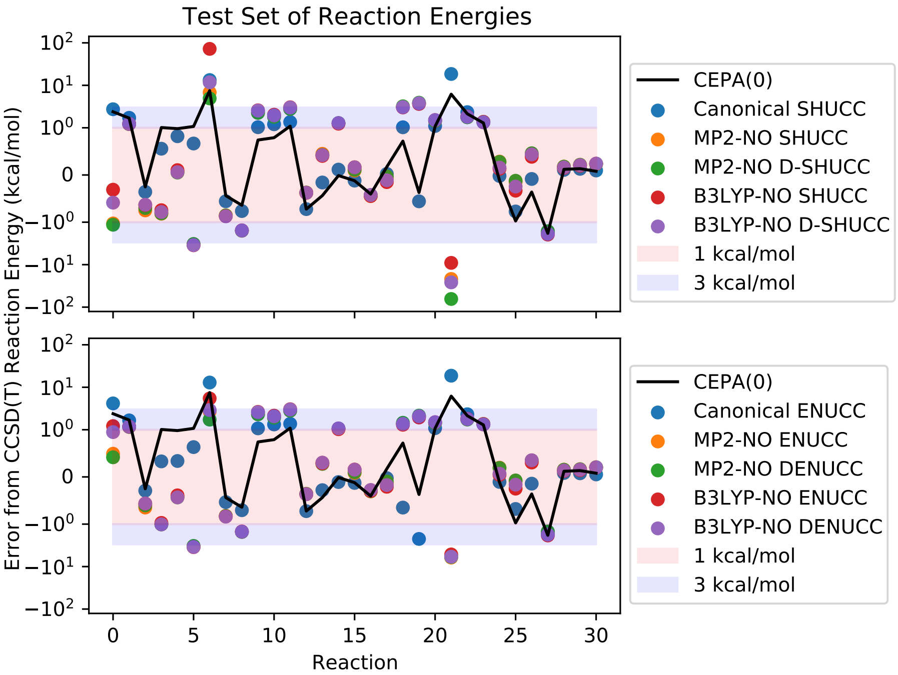
Only in ENUCC

$$\frac{1}{4}\sum_{klcd} \langle \phi_{ij}^{ab} | \hat{H}_N | \phi_{kl}^{cd} \rangle \, t_{cd}^{kl} - \boxed{2} \langle ij || ab \rangle \, (t_{ab}^{ij})^2 = - \langle ij || ab \rangle$$

Understanding ENUCC

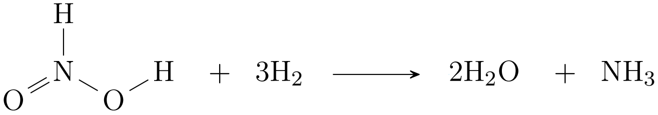
- ENUCC's ability to handle HF dissociation is consistent with Malrieu's analysis- averaged (or 0) corrections to the EPVs fail for degenerate cases, even in single bond breaking
- Aside from the factor of 2, the comparison breaks down when one notes that ENUCCD and LCCD family of methods have different energy expressions for their stationary wavefunctions:

$$E_c = \frac{1}{4}\sum_{ijab}\left(\langle ij||ab\rangle\, t_{ab}^{ij} + \underbrace{\boxed{\frac{2}{3}\langle ij||ab\rangle \left(t_{ab}^{ij}\right)^3}}_{\text{Only in ENUCC}} \right)$$

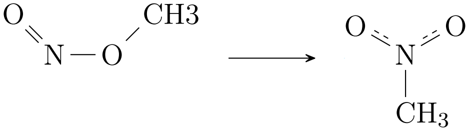

Test Set of Reaction Energies
Error from CCSD(T) Reaction Energy (kcal/mol)
Reaction
CEPA(0)
Canonical SHUCC
MP2-NO SHUCC
MP2-NO D-SHUCC
B3LYP-NO SHUCC
B3LYP-NO D-SHUCC
1 kcal/mol
3 kcal/mol
CEPA(0)
Canonical ENUCC
MP2-NO ENUCC
MP2-NO DENUCC
B3LYP-NO ENUCC
B3LYP-NO DENUCC
1 kcal/mol
3 kcal/mol

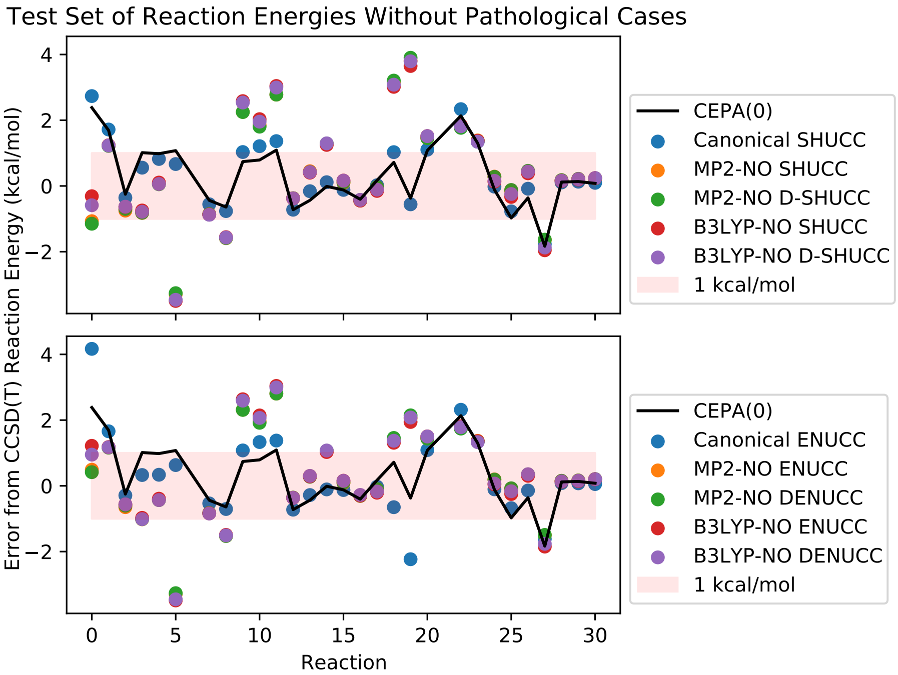
Pathological Reactions

1. Reductive Cleavage of Multiple Bonds in Nitrous Acid:



2. Isomerization of Methyl Nitrite into Nitromethane:





Test Set of Reaction Energies Without Pathological Cases
Error from CCSD(T) Reaction Energy (kcal/mol)
Reaction
CEPA(0)
Canonical SHUCC
MP2-NO SHUCC
MP2-NO D-SHUCC
B3LYP-NO SHUCC
B3LYP-NO D-SHUCC
1 kcal/mol
CEPA(0)
Canonical ENUCC
MP2-NO ENUCC
MP2-NO DENUCC
B3LYP-NO ENUCC
B3LYP-NO DENUCC
1 kcal/mol

Apparent Conclusions

- SHUCCSD and LCCSD have similar weaknesses
- ENUCCSD can help with degeneracies, but still struggles with breaking double bonds
- It might be possible to formulate it as a CEPA variant which only includes one EPV term per determinant
- The disentangled variant does not appear to generally improve accuracy, but does give a size-consistent, Hermitian functional for arbitrary orbitals